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REMARKS

Claims 19-31 and 33-39 are now in the application. Claim 19 has been amended to recite “polishing both metal and dielectric material at substantially the same polishing rate” previously recited in claim 32. Claim 19 has also been amended to recite “metal and dielectric material” in place of “surface” for purposes of consistency due to reciting “polishing both metal and dielectric material at substantially the same polishing rate”. Claim 32 has been cancelled in view of the amendment to claim 19 and claim 33 has been amended to depend from claim 19 in place of now cancelled claim 32. The amendments do not introduce any new matter or new issues since the amendments are from prior claim 32.

Claims 19-24, 26-27, 32-33 and 37-38 were rejected under 35 U.S.C. § 102(b) as being unpatentable under U.S. Patent 5,770,103 to Wang, *et al.* (hereinafter also referred to as “Wang”). Wang does not anticipate the present invention. By way of background, the present invention relates to a method for polishing a surface and especially those surfaces employed in microelectronics. The method of the present invention employs a slurry composition that is capable of polishing both metal and silicon dioxide at substantially equal rates (see page 1, lines 7-9). The slurry compositions employed in the method of the present invention comprise abrasive particles and an oxidizing agent having a static etch rate on metal of less than 1000 Å per hour and having a pH of about 5 to about 11.

As discussed in the specification, the present invention provides a method that is capable of removing the topography and scratches created during the polish of a prior level of metallization.

In the manufacture of a semiconductor device, the wires for the chip in the “back end of the line” (BEOL) are usually formed by the so-called cloisonné process. In this process, the metal is uniformly deposited on the wafer, patterned with a mask, and then etched with a plasma reactive ion etch (RIE) tool to leave the metal isolated in regions where one desires the wires. Then the dielectric material is deposited, and polished using chemical mechanical planarization (CMP) to leave the conductors properly separated. One of the benefits of this process of forming the wires is that since the plasma RIE removes material on a “line of site”, it is affective in removing the metal that might be deposited in topography that originated from a process

operation at a prior level.

However, to both reduce cost and to utilize different, low-resistance materials for the construction of the metal wires, the cloisonné process is being replaced by the damascene process to form the wires in the BEOL. In this reverse process, the dielectric is first uniformly deposited, patterned with a mask and etched. Then the metal conductor is uniformly deposited such that it forms a conformal film over the entire wafer and fills the patterns that have been etched into the dielectric. Then, using CMP, the excess surface metal is removed to leave the wires filled with metal. One of the problems with this process is since the metal is removed via CMP, which planarizes as it removes the excess material, residual metal can remain in topography that has been created at prior levels. That is, if there is a scratch or erosion in the dielectric, the metal will fill that void and cannot be removed easily via CMP without considerable over polish and the resulting damage that it introduces.

A specific example where this change in methodology of creating the wires is necessary is the manufacture of semiconductor devices with copper BEOL wiring. Since there is no viable process for etching copper currently available, it is a preferred technique to form the lines with the damascene process. In such a case, the local wiring of the semiconductor devices (that is at the lowest levels of the chip), usually utilizes tungsten as the conductor, which is then connected to the more global wiring in the BEOL, which is made of copper. In this specific example, it is found that erosion or scratching of the oxide dielectric at the last tungsten level replicates up and to the ensuing copper levels. The areas of erosion then lead to “puddles” of residual copper, and the scratches leave “stringers” of the copper, each of which if not removed at the copper CMP step would cause short-circuits. If these puddles or stringers are removed during the copper CMP step, it adds considerable processing time for the “overpolish.”

Since the removal of all of the surface metal is essential to eliminate the short circuits and because the damascene process is sensitive to both the material and underlying topography of those materials, it is clear that the surface of the wafer must be highly planar (i.e., no existing topography) prior to the deposition of the metal. The obvious method of achieving this polarity is to polish the dielectric into which the metal will be inlaid to create a smooth, scratch-free film prior to metal deposition. However, this has the disadvantage that it would necessitate additional

process steps (polishing and cleaning) and would result in a highly variable dielectric, and hence, conductor thickness. This would cause the undesirable result of having a variable resistance for the circuit.

The present invention overcomes problems in the prior art. More particularly, as discussed above, the present invention employs a slurry composition that is capable of removing the topography and scratches created during the polish of a prior level metallization. The slurry composition employed according to the present invention, as discussed above, can polish both metal and silicon at equal or substantially equal rates.

Wang fails to anticipate the present invention, since among other things, Wang fails to suggest selecting a pH of about 5 to about 11 along with selecting an oxidizing agent having a static etch rate on metal of less than 1000 Å per hour. On the other hand, Wang suggests employing a slurry having a pH of 1 to about 7 and employing an oxidizing agent such as nitrates, iodates, chlorates, perchlorates, chlorites, sulphates, persulphates, peroxides, ozonated water and oxygenated water. Many of these oxidizing agents exhibit etch rate significantly greater than that recited in the claims. Moreover, none of the examples in Wang employ a slurry composition having a pH of at least about 5 along with an oxidizing agent having a static etch rate on metal of less than 1,000 Å per hour. It has been found according to the present invention that both the pH and type of oxidizing agent, are judiciously selected in order to achieve the results obtainable by the present invention and namely to obtain polishing of both metal and silicon dioxide at equal or substantially equal rates.

On the other hand, the polishing compositions and technique suggested by Wang result in achieving much higher metal etching rates. For instance, Wang has polishing rates of nearly 4000 Å/minute (calculated from their film stack divided by polish time in example 1 and 2) which is obtained by having a high chemical component of the slurry, which is true for the pH range discussed in the examples (<5).

Contrary to the objectives of Wang, the purpose of the slurry used in the present invention is to keep the W rate low, and to make the W:BPSG selectivity = 1, by adjusting the pH higher than other slurries. According to the present invention, the pH is between 5 and 11 to make the selectivity equal or substantially equal. Needless to say, the tungsten polishing rate

according to the present invention is also a factor of about 20 less than that desired by Wang

The objective of Wang is to achieve very high polishing rates for metal as contrasted to the results obtainable by the present invention. The objective of Wang is to provide a slurry for removing titanium and other metals while suppressing the rate of removal of silicon (for instance, see column 3, lines 1-7 thereof). To etch metal and silicon dioxide at substantially the same rate would be contrary to the desires of Wang.

In addition, the claims now recite “polishing both metal and dielectric material at substantially the same polishing rate” from prior claim 32, which as recognized by the Examiner is not taught by Wang. Moreover, as discussed above this effect would be contrary to the objectives of Wang.

Furthermore, the process constituents such as the abrasive and the oxidizing agent used by Wang, *et al.* are not identical to those claimed since nothing in Wang leads to employing a composition having the same abrasive, oxidizing agent, and pH as recited in the present claims from all of the possible combinations included within the suggestions of Wang.

It seems that this rejection is based on the assumption that premised that chemistry of the slurries of Wang and the present invention are similar enough to resume the static etch rates are likewise similar. Such a presumption is in error and at best merely speculative (and quite often wrong) because of the presence of particles in a slurry. When dealing with slurries, the situation is more complex. For instance, it is known that slurries, with their large surface area for adsorption, behave very unpredictably and differently and specifically are very sensitive to pH and the material properties of the abrasive. It is also well known that the surface charge tends to drive this difference. It is known that the iso-electric point can be quite different between particles--even particles that are manufactured via different means. (For example, see GA Parks, Isoelectric Point of Solid oxides, Chemical Reviews, 1965 pp 177-198, copy attached). In fact, Wang's description states this effect explicitly, when discussing the complexation of various salts and organics to SiO₂ to affect polishing rate (Column 2, line 42-65 and Column 3, line 5).

Wang fails to anticipate the present invention. In particular, anticipation requires the disclosure, in a prior art reference, of each and every recitation as set forth in the claims. See

Titanium Metals Corp. v. Banner, 227 USPQ 773 (Fed. Cir. 1985), Orthokinetics, Inc. v. Safety Travel Chairs, Inc., 1 USPQ2d 1081 (Fed. Cir. 1986), and Akzo N.V. v. U.S. International Trade Commissioner, 1 USPQ2d 1241 (Fed. Cir. 1986).

There must be no difference between the claimed invention and reference disclosure for an anticipation rejection under 35 U.S.C. 102. See *Scripps Clinic and Research Foundation v. Genetech, Inc.*, 18 USPQ2d 1001 (CAFC 1991) and *Studiengesellschaft Kohle GmbH v. Dart Industries*, 220 USPQ 841 (CAFC 1984).

Also, Wang lacks the necessary direction or incentive to those of ordinary skill in the art to render a rejection of the claims under 35 USC 103 sustainable. Wang fails to provide the degree of predictability of success of achieving the properties attainable by the present invention needed to sustain a rejection under 35 USC 103. See *Diversitech Corp. v. Century Steps, Inc.* 7 USPQ2d 1315 (Fed. Cir. 1988), *In re Mercier*, 187 USPQ 774 (CCPA 1975) and *In re Naylor*, 152 USPQ 106 (CCPA 1966).

Moreover, the properties of the subject matter and improvements which are inherent in the claimed subject matter and disclosed in the specification are to be considered when evaluating the question of obviousness under 35 USC 103. See *Gillette Co. v. S.C. Johnson & Son, Inc.*, 16 USPQ2d. 1923 (Fed. Cir. 1990), *In re Antonie*, 195, USPQ 6 (CCPA 1977), *In re Estes*, 164 USPQ (CCPA 1970), and *In re Papesch*, 137 USPQ 43 (CCPA 1963).

No property can be ignored in determining patentability and comparing the claimed invention to the cited art. Along these lines, see *In re Papesch*, supra, *In re Burt et al*, 148 USPQ 548 (CCPA 1966), *In re Ward*, 141 USPQ 227 (CCPA 1964), and *In re Cescon*, 177 USPQ 264 (CCPA 1973).

Furthermore, the law is well settled that claiming of a more specific range within a more generic range and/or claiming species from a broader group of possible compounds avoids the invention from being exactly the same as the prior art. The test employed is whether the claims read on the prior art disclosure, not on what the references broadly teach.

For example, see *Akzo N.V. v U.S International Trade Commissioner*, 1 USPQ2d. 1241 (Fed. Cir. 1986). In *Akzo*, claims that were drawn to a process for making aramid fibers using a

98% sulphuric acid were not anticipated by reference using a concentrated sulfuric solution but which did not specifically disclose that it was a 98% concentrated sulfuric acid solution.

The Court further found that no anticipation exists when one would have to “randomly pick and choose a number of different polyamides, a plurality of solvents and a range of inherent viscosities” to reach the claimed invention.

In *Rem-Cru Titanium v. Watson*, 112 USPQ 88 (D.D.C.-1956), the prior art showed alloys having broad ranges which included the claimed ranges. However, the prior art did not specifically disclose the more limited claimed ranges or alloys having the characteristics of the claimed alloy, which is analogous to the present case. Accordingly, the Court held the claims to be allowable. For a similar fact pattern and same holding, please see *Becket v. Coe* (CA, DC 1938) 38 USPQ2 and *Terak v. Watson* (DC-DC 1954) 103 USPQ78. Also, see *Minnesota Mining & Manufacturing Co. v. Johnson & Johnson Ortho-Paedics, Inc.* (24 USPQ2d, 1321 Fed. Cir. 1992). Here the Court held that although the claims may be subsumed in a prior art reference generalized disclosures, this is not literal identity. The reference ranges provided no guidelines on how to construct a product with the inventions attributes.

An invention cannot be rejected based on inherency because of probability of possibilities of the presences of the constituents in the prior art. See *Crown Operations International, Ltd. v. Solutia*, 24 USPQ2d 1917 (Fed. Cir. 2002).

Also, Wang is to be considered as a whole, and portions arguing against or teaching away from the claimed invention must be considered. See *Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve, Inc.* 230 USPQ 46 (Fed. Cir. 1986). It is improper to take portions of a disclosure out of their proper context. See *Bausch & Lomb, Inc. v. Barnes-Hind/Hydrocurve, Inc.*, *supra*.

The rejection of Claims 19-25, 28-31, 34-36 and 39 rejected under 35 U.S.C. § 102(e) as being anticipated by over U.S. Patent 5,804,518 to Sakatani, *et al.* (referred to herein as “Sakatani”) has been overcome by the above amendment to claim 19 to include recitations from prior claim 32. Claim 32 was not rejected over Sakatani.

The Examiner is respectfully requested to enter this Amendment After Final, in that it

raises no new issues, but merely places the claims in a form more clearly patentable over the references of record. In the alternative, the Examiner is respectfully requested to enter this Amendment After Final in that it reduces the issues for appeal.

The Director is hereby authorized to charge any fees, or credit any overpayment, associated with this communication, including any extension fees, to CBLH Deposit Account No. 22-0185.

Date: 3-17-04

Respectfully submitted,

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NO. 1980 P. 2/23

**THE ISOELECTRIC POINTS OF SOLID OXIDES,
SOLID HYDROXIDES, AND AQUEOUS HYDROXO COMPLEX SYSTEMS**

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Received September 9, 1964

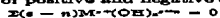
CONTENTS

I. Introduction.....	177
II. The Isoelectric Points of Solid Oxides and Hydroxides.....	178
A. Selection and Presentation of Data.....	178
1. General.....	178
2. Aluminum Oxides and Hydroxides.....	178
3. Quartz and Silica Gels.....	178
B. Variables Affecting the Isoelectric Point.....	178
1. Gross Effect of Cationic Charge.....	178
2. Effects of Hydration.....	184
3. Effects of Impurities.....	185
4. Nonstoichiometry, Defect Structures, and Semiconductors.....	188
C. Variation of IEPs with Cationic Size and Charge.....	188
1. An Electrostatic Model.....	188
2. Coordination Number Six and Crystal Field Effects.....	189
3. Coordination Number Four.....	190
4. Coordination Number Eight.....	190
5. Summary.....	190
III. The Isoelectric Points of Aqueous Hydroxo Complex Systems.....	191
IV. Comparison of the Isoelectric Points of Solids with Those of Hydroxo Complex Systems.....	192
A. General Observations.....	192
B. Adsorption and Identification of Potential-Determining Species.....	192
C. Alternate Mechanisms for Potential-Determining Ion Adsorption.....	194
1. Adsorption onto Hydrogen-Bonded Water.....	194
2. Nonequivalence of Potential-Determining Species.....	196
5. pH-Dependent Surface Modification.....	196
V. Summary and Conclusions.....	196
VI. References.....	196

I. INTRODUCTION

Solid oxides in aqueous suspension are generally electrically charged as may be observed most directly in electrophoretic experiments. The charge has long been attributed to one of two apparently indistinguishable mechanisms (3-7, 36, 56, 81, 87, 129): (a) amphoteric dissociation of surface MOH groups; and (b) adsorption of metal hydroxo complexes derived from the hydrolysis products of material dissolved from the solid, i.e., from amphoteric dissociation of $M^{++}(OH)_2$ (aq).

Both mechanisms explain qualitatively the pH dependence of surface charge and the existence of a pI resulting in zero net charge, called the isoelectric point (IEP) or zero point of charge (ZPC). The term "isoelectric point" is variously used to represent both the pI at which an immersed solid oxide surface has zero net charge and the pI resulting in (electrically) equivalent concentrations of positive and negative complexes, i.e.,



in a system of hydroxo complexes, $M^{++}(OH)_2$.

The term "IEPS" will be used when referring to solids and "IEP" when referring to dissolved species. The IEPS and the ZPC are identical by definition.

Based primarily on data for the W(VI) and Fe(III) systems it was proposed in 1952 (87) that the IEPS was identical with the IEP of the corresponding hydroxo complexes. The evidence readily available at that time was convincing but meager. A much more extensive collection of IEPS's and IEP's has been compiled to serve as a reference list and to test whether or not the two are indeed equal.

This paper is concerned first with the isoelectric points of solid oxides and an analysis of the dependence of the IEPS on the properties of the cation, its coordination, the hydration state of the solid, and its purity. The second major concern of the paper is comparison of the IEPS's with the isoelectric points of appropriate hydroxo complex systems and a discussion of the relationship between the two.

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 3/23

178

GEORGE A. PARES

II. THE ISOELECTRIC POINTS OF SOLID OXIDES AND HYDROXIDES

A. SELECTION AND PRESENTATION OF DATA

1. General

Many methods have been used to estimate the IEPs. Electrokinetic methods, including electroosmosis, streaming potential, and electrophoresis, are used commonly enough to require no further description. Direct measurement of potential-determining ion adsorption by potentiometric titration (10, 83a, 87) and study of the pH dependence of nonspecific adsorption are important, less commonly used methods. The IEPs may be inferred from a great variety of other measurements because much of the behavior of near-colloidal suspensions depends upon the structure of the electrical double layer which is absent or collapsed at the IEPs (88a, 129).

All of the IEPs data available to the author are summarized in Table I. The entries listed under each element are arranged chronologically, the most recent first. Whenever possible, details of sample preparation and characterization, measurement method, and experimental conditions are given. In one case details are sufficiently complex to merit special mention. Matteson and Fugh (72) prepared hydrous oxides by mixing appropriate metal salts, usually the chloride, and HCl or NaOH as necessary to vary pH in resulting suspensions. Electrophoretic velocities were measured in the same suspension after aging for approximately 12 hr. Thus the material for which the IEPs is reported has been precipitated at the IEPs and still contains whatever coprecipitated anions were present during precipitation. No attempt was made to identify the solid by X-ray diffraction. Only in the case of Al_2O_3 and Fe_2O_3 were the solids chemically analyzed.

IEPs are considered questionable for any reason are set off in parentheses. In general, all of the IEPs listed in Table I are used in the analyses to follow. However, the most basic IEPs for ZrO_2 and TiO_2 are omitted because of the high probability that specific adsorption of cations has occurred in these cases. The IEPs of $Mn(OH)_2$ and $Sr(OH)_2$ are omitted because special precautions should be taken to prevent oxidation of the hydroxides, and no such precautions are mentioned by the experimenter.

Many IEPs citations were found for the four oxide systems $Al(III)$, $Fe(III)$, $Si(IV)$, and $Ti(IV)$. When the frequency of recurrence of an IEP among independent citations for each well-characterized material was studied ("citation frequency analysis"), several clusters of values were observed. Although, by definition, one IEP characteristic of each different material would be expected, the average of each cluster (which includes two or more independent citations) is taken as a significant apparent IEPs for the material. This is done

because the high frequency of recurrence of the "cluster values" seems to indicate that each does indeed have real meaning. Detailed citations for each system are given in Tables II, III, IV, and V.

2. Aluminum Oxides and Hydroxides

IEPs for "amorphous" $Al(OH)_3$, "hydrous" Al_2O_3 , and for well-characterized α and γ forms of Al_2O_3 , $AlOOH$, and $Al(OH)_3$ are given in Table II. A citation frequency analysis of the IEPs reported for each material was made. Replicate measurements on one material in the same laboratory were considered once. Measurements on one material in one laboratory but by several methods were considered independent.

Robinson, Paak, and Fuersteman (108) have shown that heat treatment of synthetic $\alpha-Al_2O_3$ decreases the IEPs to a value near pH 8.7. Subsequent aging for 7 days under water led to values near 9.2. Holmes (86) found an intermediate value after an indefinite water-aging time (≤ 1 day); hence, his value was rejected as falling to represent any equilibrium state of the solid. The observations on natural minerals by Schuylenborgh and Sanger (111, 112) have not been reproduced by any other group, hence are questioned but not rejected, because their method is valid (1) and IEPs for many of their synthetic materials agree with observations by others.

IEPs determinations on amorphous materials are accepted only with reservation owing to the uncertainty of structure and to the very high probability of anion coprecipitation (124). When first precipitated, cold amorphous aluminum hydroxide is probably hydrous $\gamma-AlOOH$. On aging cold, transition from $\gamma-AlOOH$ to $\alpha-AlOOH$ and to $\alpha-Al(OH)_3$ occurs. On aging hot ($\sim 100^\circ$), $\gamma-AlOOH$ crystals grow and lose adsorbed water. Thus amorphous materials are probably mixtures of hydrous γ - and $\alpha-AlOOH$ and $\alpha-Al(OH)_3$ (124). The average IEPs (of cluster averages) for each oxide and hydroxide of aluminum are summarized in Table I. Further discussion of these materials will appear under "Hydration" and "Effects of Impurities" below.

3. Quartz and Silica Gels

IEPs citations for SiO_2 are listed in Table IV. Excluding citations stating that the IEPs is less than "X" pH, natural quartz has an average IEPs of pH 2.2 and gels and sols an average of pH 1.8. The difference is probably not significant, hence an IEPs less than or equal to pH 2.0 \pm 0.2 should be assumed.

B. VARIABLES AFFECTING THE ISOELECTRIC POINT

1. Gross Effects of Cationic Charge

Broad probable IEPs ranges characteristic of the cation oxidation state may be selected from Table I as shown in Chart I.

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NO. 1980 P. 4/23

ISOELECTRIC POINTS OF SOLID OXIDES AND HYDROXIDES

179

Material	IEPS	ISOELECTRIC POINTS OF OXIDES AND HYDROXIDES**		Investigator	Ref.
		Aluminum	Others		
$\alpha\text{-Al}_2\text{O}_3$ $\gamma\text{-Al}_2\text{O}_3$ $\gamma\text{-AlOOH}$ $\gamma\text{-Al(OH)}_3$	0, 0, 0, 0.2 (5.0) (7.7), 0.1 0.0 0.25	See Table II			
Sb_2O_3	(<0.4)	Antimony un, IEPS by eo		Michaels	75
BeO (hydrous)	(10.2)	Beryllium un, IEPS by eo		Michaels	75
Cd(OH)_2	(>10.0)	Cadmium un, ppt. from $\text{CdCl}_2 + \text{KOH}$, w, a, prod- uct Cd(OH)_2 , or CdO(hyd) , IEPS by map.		Holmes	86
CdO	(10.4 \pm 0.2)	Cd(OH)_2 , ig., a (contains ~6% Cd_2SiO_4 , $2\text{H}_2\text{O}$), IEPS by map.		Holmes	86
CeO_2 (hydrous)	(6.75)	Cerium un, ppt $\text{CeCl}_3 + \text{NaOH}$, IEPS by map, in μ est. = 0.02 M		Matteson and Fugh	72
Cr_2O_3 (hydrous)	(7.0)	Chromium ppt. $\text{CrCl}_3 + \text{NaOH}$ as descr. IEPS by map. If 10% excess NaOH : w, IEPS = 0.40; w, a (4 mo. at room temp.), IEPS = 0.90; w, a (temp. > room temp.), IEPS = 7.15. If stoichi- ometric: w, IEPS = 0.68; w, a (4 mo. at room temp.), IEPS = 6.90; w, a (temp. > room temp.), IEPS = 7.18. If 10% deficient NaOH : w, IEPS = 7.10; w, a (4 mo. at room temp.), IEPS = 7.20; w, a (temp. > room temp.), IEPS = 7.40		Tewart and Ghosh	110
Co(OH)_2	(~11.4)	Cobalt un, ppt $\text{CoCl}_2 + \text{NaOH}$, IEPS by map. in μ est. = 0.01 M		Matteson and Fugh	72
1. Cu(OH)_2 CuO	(9.4 \pm 0.4) 9.5 \pm 0.4	Copper Blue ppt from $\text{Cu(NO}_3)_2 + \text{NaOH}$ (0°) (identified by color only, w (0°), a (0°)) un, IEPS by map. (0°) w, a (100°), a, IEPS by map. (room temp.)		Holmes	86
2. Cu(OH)_2 (hydrous)	(7.6)	un, ppt $\text{CuCl}_2 + \text{NaOH}$, IEPS by map. in μ est. \leq 0.01 M		Matteson and Fugh	72
1. Fe(OH)_2 2. Fe_2O_3	(12 \pm 0.5) 6.5 \pm 0.2	Iron un, IEPS by eo Natural magnetite (Fort Henry, N. Y.), dry ground only, IEPS by map.		Krause and Borkowska Iwasaki, Ogoke, and Kim	84 84
3. Fe_2O_3 4. $\alpha\text{-Fe}_2\text{O}_3$ $\gamma\text{-Fe}_2\text{O}_3$ $\gamma\text{-FeOOH}$ $\gamma\text{-Fe(OH)}_3$ (amorph)	6.5 \pm 0.2 0.2, 0.7, 8.0 0.7 \pm 0.2 0.7 \pm 0.2 7.4 8.5	See Table III			
La_2O_3 (hydrous)	(10.4)	Lanthanum un, ppt $\text{LaCl}_3 + \text{NaOH}$, IEPS by map. at μ est. = 0.01 M		Matteson and Fugh	72

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 5/23

180

GEORGE A. PARR

Material	IEPS	Comment	Investigator	Ref.
TABLE I (Continued)				
Lead				
1. $\text{Pb}(\text{OH})_2$	(9.8 \pm 0.5)	un, white ppt dil. $\text{Pb}(\text{NO}_3)_2$ + NaOH , w, s, $\text{Pb}(\text{OH})_2$ + H_2CO_3 , $\text{Pb}(\text{OH})_2$ (s), gave ZPC = 11.0 \pm 0.2, IEPS by mep.	Holmes	80
2. $\text{Pb}(\text{OH})_2$	(11.0)	un, ppt $\text{Pb}(\text{NO}_3)_2$ + NaOH , IEPS by mep. at μ est. <0.01 M	Mattson and Fugh	72
Magnesium				
1. MgO	12.4 \pm 0.3	Optical grade MgO (Magnovite, Norton Co.) w, d, IEPS by mep.	Robinson, Fask, and Puerstener	103
2. $\text{Mg}(\text{OH})_2$	(~12)	un, ppt MgCl_2 + NaOH , IEPS by mep. in μ est. <0.01 M	Mattson and Fugh	72
3. $\text{Mg}(\text{OH})_2$	(~12)	un, IEPS by eo	Michaels	78
Manganese				
1. $\text{Mn}(\text{OH})_2$	(7.0)	un, ppt MnCl_2 + NaOH , IEPS by mep. at μ est. <0.01 M	Mattson and Fugh	72
2. MnO_2	(4-4.5)	Synth. lg. $\text{Mn}(\text{NO}_3)_2$ in air, s (HNO_3), w, d (100°), mole ratio $\text{O}/\text{Mn} = 2.08$, tetrag. MnO_2 (s), IEPS by drift	Rao	98
HgO	7.3 \pm 0.3	ppt $\text{Hg}(\text{NO}_3)_2$ + NaOH , μ , w, IEPS by mep.	Holmes	80
Nickel				
1. NiO	10.3 \pm 0.4	Baker and Adamson reagent, NiO , IEPS by mep.	Holmes	80
2. $\text{Ni}(\text{OH})_2$	11.1 \pm 0.4	ppt $\text{Ni}(\text{NO}_3)_2$ + NaOH , w, s, IEPS by mep.	Holmes	80
3. $\text{Ni}(\text{OH})_2$	(~12)	un, ppt NiCl_2 + NaOH , IEPS by mep. in μ est. ~ 0.01 M	Mattson and Fugh	72
Platinum				
PtO_2	(2-14)	Supposed oxide film on Pt in 1 atm. O_2 , IEPS est. from pH dependence of Pt- O_2 electrode.	Kruyt	83b
Plutonium				
1. PuO_2	9.0	Sulfate lg. (850°), IEPS by mep.	Bowden and Francis	118
2. PuO_2	8.8-8.9	Oxalate lg. (800-900°), ground, IEPS by mep.	Bowden and Francis	118
Silicon				
1. SiO_2	2.2	Natural α - SiO_2 (quartz)	See Table IV	
2. SiO_2 (hydrous)	1.8	SiO_2 sols and gels		
Thorium				
1. ThO_2	9.0-9.3	ppt oxalate from nitrate at room temp. to 70°, lg. (900-1100°), grind, IEPS by mep.	Bowden and Francis	118
2. ThO_2	(8.5-11)	un, ppt $\text{Th}(\text{NO}_3)_4$ + NaOH , w, d (100°), IEPS est. add. (Na^+ , Cl^-)	Amphlett, MacDonald, and Redman	3
3. ThO_2	(9.5)	ppt oxalate from nitrate, lg. (20 hr. at 400° then 70 hr. at 900°), store CO_2 free, IEPS by mep. in μ indic.	Anderson	6
	(8)	$\mu = 10^{-4}$ M KCl , uncertain only because IEPS est. by scaling figure		
	(4.2)	$\mu = 10^{-4}$ M KCl		
4. ThO_2	(6.8)	un, ppt $\text{Th}(\text{NO}_3)_4$ + NaOH , IEPS by mep. in est. $\mu \sim 0.04$ M	Mattson and Fugh	72
Tin				
1. SnO (hydrous)	(6.6)	un, ppt SnCl_2 + NaOH , IEPS by mep.	Mattson and Fugh	72
2. SnO_2	7.8	Natural cassiterite, s, w, d (120°), IEPS by mep.	Johansen and Buchanan	56
3.		SnO_2 synth. HNO_3 + $\text{Sn}(\text{metal})$ 80°, product w	Johansen and Buchanan	56

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 6/23

ISOELECTRIC POINTS OF SOLID OXIDES AND HYDROXIDES

181

Ref.	Material	IEPS	TABLE I (Continued)		Investigator	Ref.
			Comment	Comment		
10	SnO ₂ (hydrous)	4.6	IEPS by map, material as down.			
	SnO ₂	5.8	SnO ₂ (hyd) in (800°, 2 hr. in air), IEPS by map.			
12	4. SnO ₂	(8.8)	Mineral cassiterite, a, w, d (120°), IEPS by sp.		Johansen and Buchanan	55
	5. SnO ₂		Three natural cassiterites g, w, d (110°), IEPS by sp.		O'Connor and Buchanan	70
10		4.7	74.6% Sn, low Fe			
		(9.5)	75.6% Sn, high Fe, "soluble base" present			
72	6. SnO ₂ (hydrous)	4.7	75.4% Sn, low Fe			
		(9.0)	un, ppt SnCl ₂ + NaOH, IEPS by map. in est. $\mu \sim 0.01 M$		Matteson and Pugh	72
15			Titanium			
	1. TiO ₂	(9.5), 4.7	Natural rutile			
	2. TiO ₂	4.7, 6.3	Synthetic rutile, anatase			
16			Tungsten			
	1. WO ₃ (hydrous)	(0.6)	ppt Na ₂ WO ₄ + HCl, IEPS by map.		El Wakkad and Risk	27
	2. WO ₃ (hydrous)	(<0.3)	un, IEPS by so		Michaels	75
16			Uranium			
	1. UO ₂ -U ₂ O ₅		Samples synth. thermal decomp. ammonium diuranate + H ₂ -H ₂ O(g) mixt. at temp. indic. ground, w, IEPS by sp.		Pravdic and Sotman	96
10		5.8 \pm 0.2	ig. (800°), cool in 8 hr., oxygen to uranium			
10		4.7 \pm 0.2	mole ratio (O/U) = 2.00, str. cubic by x			
10		6.6 \pm 0.3	ig. (800°), water quenched, O/U = 2.00			
72		6.0 \pm 0.2	ig. (800°), O/U = 2.03, cubic by x			
		5.0 \pm 0.2	ig. in air to U ₂ O ₅ , then in H ₂ -H ₂ O to O/U = 2.45			
187	2. UO ₂ -U ₂ O ₅	3.0 \pm 0.2 and 4.5 \pm 0.5	Two samples of natural uraninite, O/U = 2.3 ground, w, a, IEPS by sp (see also Figure 1)		Ferreira and Ottewill	88
	3. U ₂ O ₅	(4)	Synth. w, a, IEPS by sp		Ferreira and Ottewill	88
18	Y ₂ O ₃ (hydrous)	(8.98)	un, ppt Y(NO ₃) ₃ + NaOH, IEPS by map.		Matteson and Pugh	72
10			Zinc			
	1. ZnO		ppt ZnCl ₂ + NaOH at 100°, refluxed with H ₂ O 10 days, w, x, w SiO ₂ major impurity, IEPS by u		Ray and de Bruyn	101
		2.2	$\mu \leq 10^{-3} M NaCl$			
		8.7	$\mu \leq 10^{-3} M NaNO_3$			
18	2. ZnO	(9.0 \pm 0.3)	Oxidized zinc metal, IEPS by drift		Hasegawa and Fréssyaka	48
	3. ZnO	9.3 (9.2-9.7)	ppt Zn(NO ₃) ₂ + NaOH, w, a, x, IEPS by map.		Holmes	50
8	4. ZnO (hydrous)	(10.3)	un, ppt ZnCl ₂ + NaOH, IEPS by map.		Matteson and Pugh	72
6			Zirconium			
	1. ZrO ₂	(10-11)	un, ppt ZrO(NO ₃) ₂ + NaOH, w, d (100°), IEPS est. ads. (Na ⁺ , Cs ⁺ , Cl ⁻)		Amphlett, Macdonald and Redman	5
	2. ZrO ₂	(4)	un, natural mineral, IEPS by so		Farver	128
	3. ZrO ₂ (hydrous)	(6.7)	un, ppt Zr(NO ₃) ₃ + NaOH, IEPS by map. in est. $\mu \sim 0.02 M$		Matteson and Pugh	72

* Abbreviations: ads., IEPS estimated as pH at which adsorption of indifferent positive ions equals that of negative ions (48, 63a); a, aged or stored in distilled water for period indicated (if known); o, sample cleaned by leaching in concentrated HCl or other acid indicated; co, IEPS estimated as pH of maximum rate of coagulation of a suspension (120); d, sample dried <100° or as indicated, stored dry; dl, sample cleaned by dialysis; drift, IEPS estimated as pH at which suspension pH does not drift from that at which it was made. Usually oxide is precipitated at initial pH of test (81a); eo, electroosmosis or electroosmosis (83a); ig, sample ignited at temperature indicated; un, exact identification of solid missing. Structure or composition inferred from author's statement or sample history; map, microelectrophoresis (1, 63a); ppt, sample prepared by precipitation using solutions of salts indicated; sp, IEPS sample history; sep, microelectrophoresis (1, 63a); sub, IEPS estimated as pH of maximum subsidence rate of a coagulated suspension (129); u, IEPS estimated as pH at which adsorption of H⁺ is equal to that of OH⁻ as determined by potentiometric titration of a suspension; μ , total salt concentration during IEPS measurement; w, sample washed in water, usually by decantation, until free of Cl⁻ or SO₄²⁻, etc.; x, sample identified by X-ray diffraction; (), citations in parentheses are estimates based on insufficient or inadequately reported data or reports of experiments using poorly characterized solids. * Unless otherwise noted, the only foreign ions present in the systems reported are either Na⁺ or K⁺ and Cl⁻, NO₃⁻, or ClO₄⁻.

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 7/23

182

GEORGE A. PARKS

TABLE II
ISOELECTRIC POINTS OF ALUMINUM OXIDES AND HYDROXIDES*

IEPS	Description	Investigator	Ref.
1. 0.1-0.2	Synth. α -Al(OH) ₃ , lg. (1000-1350°), x, w, dl, a (>2 days, 0.1 M KCl), w, IEPS by sp in μ = 10 ⁻³ M KCl	Kos'mina, Belova, and Sannikov	63
2. 0.4-0.7 0.1-0.6	α -Al ₂ O ₃ , Linds A abrasive (Linds Air Products Co.) lg. (600-1400°), a (<1 day) All non-ig. and ig. (<1000°) samples after a (H ₂ O, 7 days), x, c, w, IEPS by sp, μ = 10 ⁻³ M KCl	Robinson, Pask, and Fuerstenau	103
7.7	lg. (1400°), a (H ₂ O, 7 days), etc.		
8. 0.1 9.0-9.1 9.1	Same basic material as 2 x, c, w, a (7 days), IEPS by ti, μ = 10 ⁻³ M KCl x, c, w, a (7 days), IEPS by sub, μ = 10 ⁻³ M KCl x, c, w, a (7 days), IEPS by mep., μ = 10 ⁻³ M KCl, KNO ₃ , and KClO ₄ separately	Yoppe and Fuerstenau	129
4. 7.5-8.2	Flame-fused synthetic sapphire, ground in mullite ware, not cleaned, a (<1 day), x, IEPS by mep.	Holmes	86
5. 10 9.8 \pm 0.2	"Chromatographic Al ₂ O ₃ used as received" IEPS by ads. H ⁺ , OH ⁻ IEPS by dirt	Havazyńska and Prędzyńska	48
6. 6.7	Synthetic sapphire, c, w, d (120°), IEPS by eo	Debiás, Spurný, and Freudlová	24
7. 8.4 9.4 8. (9.4)	Natural corundum, c, w, d (120°) IEPS by mep. 0.94% SiO ₂ , IEPS by sp Flame-fusion sapphire (Linds Air Products Co.), c, w, a, IEPS by sp	Johansen and Buchanan Modi and Fuerstenau Schuylenborgh and Sanger	55 76 112
9. a. 2.3 b. 3.0	Synthetic corundum Natural corundum, x, c, w, dl, d, IEPS by mep.		
1. 7.4-8.6 2. (8.0)	Synth. γ -Al(OH) ₃ , lg. (300-800°), x, w, dl, a (>2 days, 0.1 M KCl), w, IEPS by sp in μ = 0.001 M KCl γ -Al ₂ O ₃ prepared by thermal treatment and aging of the hydrolysis product of Al ethylate, IEPS by mep.	Kos'mina, Belova, and Sannikov Fricke and Keefer	63 81
1. 7.7 2. (<2) 3. 8.8 4. 8.6 (a), 7.6 (a)	Synth. Al(OH) ₃ , lg. (300°), dl, a (>2 days in 0.1 M KCl), w, IEPS by sp in μ = 0.001 M KCl, x Natural boehmite, x, dl, d, IEPS by mep. Synthetic α -AlOOH, x, w, dl, d, IEPS by mep. Synth. from AlCl ₃ + NH ₄ OH at 12° Synth. from NaAlO ₂ (a and c = 100a) + CO ₂ Synthetic boehmite, prepared by thermal treatment and aging of the hydrolysis product of purified Al ethylate, IEPS by mep.	Kos'mina, Belova, and Sannikov Schuylenborgh and Sanger Schuylenborgh Fricke and Keefer	63 112 111 81
1. (<2) 2. 7.6 3. 5.4	Natural diasporite, x, dl, d, IEPS by mep. Synthetic diasporite, x, dl, d, IEPS by mep. Synth. at 70° from AlCl ₃ + NH ₄ OH, product α -AlOOH + tr γ -Al(OH) ₃ Synth. from NaAlO ₂ + CO ₂ (g)	Schuylenborgh and Sanger Schuylenborgh	112 111
1. 3.8-5.0 2. 5.0, 5.2 3. 4.9	Synth. α -Al(OH) ₃ , (8.8) and same lg. (300°) (5.0), dl, a (>2 days in 0.1 M KCl), x, w, IEPS by sp Natural gibbsite (two samples), dl, d, IEPS by mep. Synth. by aging NaAlO ₂ (aq), dl, d, x, IEPS by mep.	Kos'mina, Belova, and Sannikov Schuylenborgh and Sanger Schuylenborgh	63 112 111
1. 9.3 \pm 0.2 2. 7.5 3. 5.4 4. 9.2	γ -Al(OH) ₃ , synth. by hydrolysis of purified Al(OC ₂ H ₅) ₃ , x, w, a, IEPS by mep. Synthetic materials, x, w, dl, d, IEPS by mep. Synth. from AlCl ₃ + NH ₄ OH(aq) at 70° Synth. from NaAlO ₂ (aq) + CO ₂ (g) γ -Al(OH) ₃ , synth. by hydrolysis of purified Al(OC ₂ H ₅) ₃ , or related compounds, IEPS by mep.	Korpi and Holmes Schuylenborgh Fricke and Keefer	86 111 81

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 8/23

ISOELECTRIC POINTS OF SOLID OXIDES AND HYDROXIDES

183

TABLE II (Continued)		Investigator	Ref.
IEPS	Description		
	In buffers IEPS shifts as follows: glycerol (6.00), borate (5.78), acetate (5.59), phosphate (4.06), citrate (2.4). Buffer concentrations not given	Friks and Leonhardt	82
	Amorphous Al_2O_3		
1.	ppt $\text{AlCl}_3(\text{aq}) + \text{NaOH}$ as described, IEPS by map. IEPS given in parentheses. If 10% excess NaOH , w (5.08), a (4 mo. room temp.) (5.78); a (temp. > room temp.) (5.70); if stoichiometric NaOH , w (5.03), a (4 mo., room temp.) (7.06); a (temp. > room temp.) (7.28); if 10% deficient NaOH , w (7.29), a (4 mo., room temp.) (7.32); a (temp. > room temp.) (7.43)	Tewari and Ghosh	120
2. 8.0	Unaged product of hydrolysis of very pure aluminum ethylate, IEPS by map.	Friks and Keefer	81
3.	ppt from AlCl_3 or $\text{Al}(\text{SO}_4)_3$ with NaOH adjusted to fix final pH. IEPS by map. without washing (see text)	Matteson	71
8.0 \pm 0.2	In solid, mole ratio $\text{Cl}/\text{Al}_2\text{O}_3$ ca. 0.005		
7.8 \pm 0.2	In solid, mole ratio $\text{SO}_4/\text{Al}_2\text{O}_3$ ca. 0.074		

* For meaning of abbreviations see footnotes, Table I.

TABLE III
ISOELECTRIC POINTS OF IRON(III) OXIDES AND HYDROXIDES*

IEPS	Description	Investigator	Ref.
	Natural $\alpha\text{-Fe}_2\text{O}_3$ (Hematite)	Jay, Watson, and Cropton	58
1.	Hematite		
5.7	IEPS by sp		
5.4	IEPS by ti		
2. (4.5-5.0)	α , w , a , IEPS by ti and suspension effect (53a)	Chirvashiak	20
3. 6.6 \pm 0.2	Specular hematite (Labrador), a , then ground in mullite ware, w , a , IEPS by map., two independent observations: 6.6, 6.7	Holmes and Tacey	80
4. 6.7 \pm 0.1	Mineral selected, ground, w , IEPS by map.	Iwasaki, Cooke, and Choi	81
5. 6.9 \pm 0.2	Same sample described under 3.a, w , a , IEPS by sp, $\mu = 10^{-4}$ M KNO_3	Korpi	50
6. (4.8)	Mineral α , w , d (120°), IEPS set from sp data	Johansen and Buchanan	55
7. 6.7	Mineral α , w , d (120°), IEPS by map.	Johansen and Buchanan	55
8. (3.2)	Mineral α , w , d , i , IEPS by map.	Schuylenborgh and Sanger	112
	Synthetic $\alpha\text{-Fe}_2\text{O}_3$		
1.	All materials synth. by 100° hydrolysis and aging under reflux conditions of $\text{Fe}(\text{NO}_3)_3$ solution, w , a , x , IEPS by ti (H^+ , OH^-) unless otherwise noted		
a. 5.7 \pm 0.1	$\mu \leq 1.0$ M, 4 determinations, once each in NaNO_3 , NaCl , NaClO_4 , Na_2SO_4 , 25°	Albrothson	2
b. 5.85 \pm 0.2	0.005 M NaNO_3 , IEPS by suspension effect (53a)		
c. 9.04 \pm 0.03	$\mu = 0.001$ - 0.10 M KNO_3 , 25°	Korpi	50
d. 9.08 \pm 0.03	$\mu \leq 0.01$ M KNO_3 , 21°	Farks and de Bruyn	85, 87
e. 8.77	$\mu = 1.0$ M KNO_3 , 21°		
f. 8.7 \pm 0.2	$\mu = 0.01$ - 0.10 M KNO_3 , 55°		
2.	Baker and Adamson reagent grade $\alpha\text{-Fe}_2\text{O}_3$ (synth. by ignition of $\text{Fe}(\text{SO}_4)_2$ in air or O_2), w , a , x		
8.4 \pm 0.1	IEPS by ti at 21°, $\mu \leq 0.1$ M KNO_3	Farks	85
8.0 \pm 0.2	IEPS by map.	Miaw	74
3.	Baker materials synth. $\text{FeNH}_4(\text{SO}_4)_2 + \text{NH}_4\text{OH}$, w (5% NH_4NO_3), w , IEPS by map.	Johansen and Buchanan	55
8.0	ppt as described		
6.8	ppt, d , ig. (850°, 2 hr.)		
4. 1.9	Synth. α , w , d , i , d (105°), IEPS by map.	Schuylenborgh and Sanger	112
5. 3.3	Fe_2O_3 sol synth. $\text{FeCl}_3 + \text{NH}_4\text{OH}$, w , a (H_2O , 150-180° at ~6 atm.), IEPS by map.	Toelstra and Krut	121
	$\gamma\text{-Fe}_2\text{O}_3$		
1. 6.7 \pm 0.2	Synth. by ppt FeOOH , ig. to Fe_2O_3 , x (tr. $\gamma\text{-FeOOH}$), w , IEPS by map.	Iwasaki, Cooke, and Kim	84

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 9/23

184

GEORGE A. PARKS

TABLE III (Continued)

IEPS	Description	Investigator	Ref.
1. 0.1 ± 0.1	Samples, w (H ₂ O only), x, IEPS by sp, analysed	Pianingham	80
2. 0.7 ± 0.2	w (H ₂ O), w (H ₂ O), analysed, IEPS by sp	Iwasaki, Cooke, and Colombo	52
3. 3.2	Mineral, x, w, di, d (105°), IEPS by mep.	Schuylenburgh and Banger	112
4. 0.7	Colloidal -FeOOH, synth. by aging hydrous FeCl ₃ + NaOH in 2 M NaClO ₄ , IEPS by mep.	Longwell, Buser, and Feltmeyer	67
5.	Samples synth. several ways involving different reagents, concentrations, and rates. Histories leading to more ordered structures (X-ray diffraction) lead to more acid IEPS. x, w, di, d, IEPS by mep. Analyses and DTA given in original paper	Schuylenburgh, Arens, and Kok	110, 113
5.0-7.2	Sample not dried after washing		
6.0-6.8	d (60°)		
4.2-6.8	d (105°)		
1. 7.4 ± 0.2	Natural lepidocrocite, w (H ₂ O), w (H ₂ O) anal, IEPS by mep.	Iwasaki, Cooke, and Kim	54
2.	Samples synth. in several ways. Details same as item 5, under "α-FeOOH." More ordered structures give more acid IEPS	Schuylenburgh, Arens, and Kok	110, 113
5.4-7.3	Samples not dried before study		
6.0	d (60°)		
5.3-5.7	d (105°)		
1. (7)	Hydrous or Poorly Characterized Fe ₂ O ₃ and "Amorphous Hydroxides"		
2.	"Hydroxide" IEPS est. by ada. (Zn ²⁺ , Co ²⁺)	Zhabrova and Egorov	131
3. 5.5	Synth. Fe(NO ₃) ₃ + Ni(OH) ₂ , IEPS by mep.	Schuylenburgh, Arens, and Kok	110, 113
4. 0.0	w, di, not dried		
4.3	w, di, d (105°)		
5. 5.0	FeCl ₃ sol by hydrolysis FeCl ₃ , di (5 days, 60°), α, IEPS by mep.	Hasel and Ayres	47
4.	ppt from FeCl ₃ or Fe(BO ₃) ₃ with NaOH adjusted to fix pH, IEPS by mep. without washing (see text)	Mattson	73
7.2	Mole ratio Cl/Fe ₂ O ₃ in solid is 0.005		
7.0	Mole ratio SO ₄ /Fe ₂ O ₃ in solid is 0.014		
6. (5.9 ± 0.5)	IEPS by eo	Michaels	75
	* See footnotes, Table I, for abbreviations. * 99.77% Fe ₂ O ₃ , 0.08% FeO, 0.09% SiO ₂ , same material used by Korp (59). * Washed in hot alcoholic KOH, hot H ₂ O, HNO ₃ in Soxhlet extractor for 3 hr. H ₂ O in Soxhlet for 3 days, stored in dist. H ₂ O. * ≤ 0.2% insol., ≤ 0.2% SO ₄ ²⁻ , ≤ 0.005% Cu, Zn. * 2.4% SiO ₂ , 1.7% Al ₂ O ₃ , 1.8% Fe ₂ O ₃ (30). * 58.75% Fe, 2% SiO ₂ , 0.46% Mn, 10.36% H ₂ O (400°), 11.24% H ₂ O (800°). * 56.52% Fe, 10.5% SiO ₂ , 0.55% insol.		

CHART I

MO	IEPS > pH 11.5
MO	8.5 < IEPS < 12.5
MO ₂	6.5 < IEPS < 10.4
MO ₃	0 < IEPS < 7.5
MO ₄ , MO ₅	IEPS < 0.5

The ranges include oxides, hydrous oxides, oxyhydroxides, hydroxides, and superficially hydrated or hydrous oxides. The term "hydrous" will be used in a generic sense to include any or all of these materials except "anhydrous" oxides.

Several factors help to explain the broad range of IEPS in each group. Among these are differences in hydration state, purity, and cation radius. The role of each of these factors in fixing the IEPS will be discussed in the paragraphs to follow and an equation will be developed relating the IEPS to the charge to radius ratio of the cation in the pure solid.

S. Effects of Hydration

Several groups (55, 58, 80, 103, 110-113) have independently studied the relationship between IEPS and sample history and agree in their conclusions that treatment likely to lead to bulk or surface dehydration results in a more acid IEPS than is observed for materials likely to be hydrated. The data from Table I which most clearly involve materials of differing hydration state are summarized in Table VI.

The average IEPS increase accompanying hydration for the materials listed in Table VI is about two pH units. This conclusion is in apparent conflict with the results of Kos'mina, Belova, and Sannikov (68). However, their samples were aged for several days in 0.1 M HCl, and the more acid IEPS observed with increasing hydration probably reflects increasing replacement of OH⁻ by Cl⁻ as well. The effects of impurities on IEPS will be discussed in the next section.

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 10/23

ISOELECTRIC POINTS OF SOLID OXIDES AND HYDROXIDES

185

TABLE IV

ISOELECTRIC POINTS OF SiO_2 *

IEPS	Description	Investigator	Ref.
1. 1.5	Braslian crystal, ground, c (HCl in Soxhlet extractor), w (8 hr., H_2O in Soxhlet), s, IEPS by map.	Bhappu	10
1.8	Crystals from Harding Mine, N. M., ground s, w, s, IEPS by map.	Bhappu	10
2. 3.5 \pm 0.2	Natural crystals (Mont.), s, w, s, IEPS by map.	Iwasaki, Cooke, and Choi	38
3. 2.2-2.8	Quartz from a beach sand (H. E. Sargent Co.), s, w, s, IEPS by sp. IEPS = 2.5 after sample aging at test pH (52 days)	Planinigham	30
4. (2.3)	All samples Braslian crystal, ground in a fused quartz disk grinder after c (HCl), w	Li	68
2.0	IEPS by sds. (Na^+ , I^-)		
(1-2)	IEPS by sp in HCl only		
2.7-3	IEPS by sp in 10^{-2} M NaCl		
5. <3	Quartz ground, s, w, d (120°), IEPS by map.	O'Connor and Buchanan	81
6. 3.7	Braslian crystal, ground, s, w, s, IEPS by sp	Caudin and Fuerstenau	36
1. 2-3	pH of minimum gelation rate		
2. 1-2	Sols synth. $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$ (1%) + HCl for preads. pH (20°)	Moulik and Ghosh	78
1-1.5	IEPS by location of viscosity minima. Younger gels IEPS close to pH 2, older closer to pH 1	deBoer, Linssen, and Oikarue	15, 82
3. 1.3	1% SiO_2 sols, d, IEPS by map.		
2. 2.8-3	pH of minimum gelation rate	Sen and Ghosh	114
3. (-0.5)	pH of minimum gelation rate	Hickel	49
	IEPS by so	Michaels	75

* See footnotes, Table I, for abbreviations.

TABLE V

ISOELECTRIC POINTS OF TiO_2 *

IEPS	Description	Investigator	Ref.
1. 4.7 \pm 0.2	Sample from N. C., ground, w, s (tr Fe_2O_3), IEPS by map.	Feeney	86
2. 3.6 \pm 0.2	c (H_2SO_4 , HCl), w, IEPS by sp	Graham and Madoley	44
3. 4.8	c (HCl), w, d (120°), IEPS by map.	Johansen and Buchanan	56
4. 5.5	s, w, d (120°), IEPS by sp	Johansen and Buchanan	55
1. 6.7 \pm 0.1	High purity synthetic rutile (National Lead Co.) c (HCl in Soxhlet extractor), w (8 hr., H_2O in Soxhlet), s (H_2O), IEPS by sp in 10^{-2} M NaCl	Farrell and Sun	97
2. 6.0 \pm 0.3	Average observed by two operators for several samples including reagent grade TiO_2 (anatase), TiO_2 (hydrous rutile), s, s, w, s, IEPS by map.	Feeney and Holmes	86
3. 6.0	Samples synth. hydrolysis TiCl_4 at 100° hydrous rutile, w, s, IEPS by map.	Johansen and Buchanan	56
4. 4.7	As described		
4. (4.8)	d, is. (1000° in air, 3 hr.)		
	uo, synth. TiCl_4 + NaOH , IEPS by map. in 10^{-2} M (see text)	Mattson and Fugh	73

* See footnotes, Table I, for abbreviations.

[*] Lacking direct characterization of the surfaces of oxide materials used for IEPS work, it has been necessary to infer the probable hydration state from sample history.

On exposure to water an anhydrous oxide can become "hydrated" in several ways: (1) physical adsorption of water molecules including hydrogen bonding to surface oxygen ions but not dissociation; (2) chemisorption of water which dissociates, resulting in surface -MOH groups; and (3) reaction resulting in conversion to an oxyhydroxide or hydroxide, e.g., $\text{MgO} \rightarrow \text{Mg}(\text{OH})_2$ (102). Many anhydrous oxides do not

TABLE VI

Compound	IEPS	Compound	IEPS	Δ IEPS
Fe_2O_3	6.7	Fe_2O_3 (hydrous)	5.6	1.0
Al_2O_3	6.7	Al_2O_3 (hydrous)	5.3	2.5
TiO_2	4.7	TiO_2 (hydrous)	6.3	1.5

hydrate completely to produce the hydroxide. In some cases the hydroxide is thermodynamically unstable [$\text{Hg}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$], and in others the hydrated compound is stable but the reaction rate is very slow ($\text{Fe}_2\text{O}_3 \rightarrow \text{FeOOH}$ (117), $\text{Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}(\text{OH})_3$ (124), etc.). Strong ignition reduces the hydration rates by chemi-

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 11/23

186

George A. Panx

sorption for, e.g., SiO_2 (14), and by total reaction for MgO (102) and decreases the solubility. Mechanical disturbance, e.g., by grinding, leads to an amorphous or disturbed layer with increased solubility, e.g., SiO_2 (122), and increased surface hydration, e.g., Al_2O_3 (85).

If oxide precipitates form by progressive hydrolysis, polymerization, and oxidation (104, 126), it can be expected that they would retain a superficial layer of more hydrous material which would be lost only on drying and ignition. While it is well established that very high temperatures are needed to remove the last MOH groups from silica gels and that persistent MOH groups are present in other oxides (180), direct evidence of persistent hydrous films is lacking in most cases; however, there is at least some evidence for the presence of hydrous films on Fe_2O_3 (80, 87) and ZrO_2 (21) prepared by hydrolysis. For Fe_2O_3 , the solid was identified as hematite by X-ray diffraction, yet DTA and infrared absorption experiments yielded evidence for traces of FeOOH (86).

Detailed study of sample preparation for the Al(III) and Fe(III) materials for which IEPs data are summarized in Table I makes possible several generalizations.

All of the oxides and hydrous oxides of aluminum apparently slowly hydrate (in a matter of days) to the extent that at least a film of material with the properties of $\text{Al}(\text{OH})_3$ results. Amorphous $\text{Al}(\text{OH})_3$ has the same characteristics as the crystalline modifications. The IEPs characteristic of $\alpha\text{-Al}_2\text{O}_3$ at equilibrium with water is probably about pH 9.2. All other values presently available for this material seem to represent metastable or impure states.

Ignited and natural Fe_2O_3 samples appear to hydrate quickly to the extent that their surfaces have the properties of $\alpha\text{-FeOOH}$. The more basic IEPs of $\gamma\text{-FeOOH}$ can probably be attributed to the effect of the less stable structure. $\alpha\text{-Fe}_2\text{O}_3$ hydrates no further in reasonable time. $\gamma\text{-Fe}_2\text{O}_3$, prepared by hydrolysis and not subsequently dried at high temperature has the IEPs of hydrous or amorphous Fe_2O_3 and apparently retains a coating or film of hydrous material as predicted above. Fe_2O_3 with IEPs near pH 5 apparently remains hydrated to a lesser extent than FeOOH , perhaps only physically adsorbing water.

The change in IEPs accompanying changes in hydration has been interpreted in terms of the dependence of the acid strength of surface MOH groups on the $\text{O}^{2-}/\text{OH}^-$ ratio by O'Connor, Johansen, and Buchanan (80) and by Robinson, Fask, and Fuerstenau (108). Similar arguments have been used to interpret the strengths of the oxyacids, $\text{MO}_2(\text{OH})$, (77, 89). In the latter case an increase in the ratio, m/n , is said to result in an effective increase in Z/r , the ratio of cationic charge to radius, and consequently in acid strength. Increased acid strength (or decreased IEPs) could equally well be explained in terms of the increased electrostatic

bond strength which must accompany an increase in m/n (89). The original articles should be consulted for details.

3. Effects of Impurities

Purposeful investigations of the effects of impurities on the IEPs are few. Because many systems in which the IEPs is studied provide ample opportunity for contamination by adsorption or reaction, the subject is quite important. Abramson, Meyer, and Gorin (1) pointed out that the "real" IEPs could be measured only in the absence of all ions other than hydrogen, hydroxyl, and those which are components of the solid. In discussing the origin of charge on organic colloids they listed the following charging processes: (1) dissociation, particularly acid-base dissociation of surface groups such as $-\text{COOH}$, $-\text{SiOH}$; (2) specific adsorption of ions onto otherwise neutral sites (tendencies toward ion-pair formation, hydrogen bonding, and "specific interactions" such as are responsible for complex formation in solution were mentioned as possible "driving forces" for specific adsorption); (3) oriented adsorption of polar molecules such as H_2O with subsequent adsorption of ions by 1 or 2 above; (4) weak specific adsorption of ions by induced polarization of the substrate (image force bonding).

Mechanisms 2-4 may be called specific adsorption, using the term in the sense used by Grahame (45) to denote any tendency toward interaction other than the simplest electrostatic case. It is assumed that perchlorate, nitrate, and chloride ions do not interact with oxide surfaces in any specific sense and that the charging process characteristic of oxides in aqueous suspension is either acid-base dissociation or specific adsorption of metal hydroxide complexes. The effects of other ions will be classified as impurity effects.

Overbank (52a) has pointed out that specific adsorption of anions would be expected to produce a negative surface charge under conditions otherwise identical with the IEPs. Should this occur on an oxide surface, the pH at which zero surface charge was observed would be lowered; i.e., the apparent IEPs would be shifted to a more acid pH because increased H^+ adsorption would be necessary to neutralize the anion's negative charge. A structural anionic impurity would be expected to produce an acid shift as well because the $\text{M}^+-\text{anion}-\text{H}$ surface group would in most cases be a stronger acid than $-\text{MOH}$.

Both adsorbed and structural cationic impurities present before measurement of the IEPs would be expected to shift the IEPs in the direction of the IEPs of the impurity hydroxide. Extensive evidence has been given (28) for cation adsorption on silica gel by ion exchange with H^+ from $-\text{SiOH}$ sites. In addition to an IEPs shift in the direction of the appropriate oxide, slight nonequivalence of M^{++}/H^+ exchange would also

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 12/23

ISOELECTRIC POINTS OF SOLID OXIDES AND HYDROXIDES

187

TABLE VII

EFFECTS OF IMPURITIES ON IEPs

A. Structural Impurities (Present in Solid before Experiments)

Substrate	Impurity	Impurity level, mole %	Δ IEPS*	Ref.
Al ₂ O ₃ (hydrous)	SiO ₂ **	~7.4	~ -0.6	72
Fe ₂ O ₃ (hydrous)	Cl ⁻	~0.5	~0	73
Fe ₂ O ₃ (anhydrous)	SiO ₂ **	~1.4	~ -1.4	73
Fe ₂ O ₃ (hydrous)	Cl ⁻	~0.5	~ -0.2 to -0.6	74, 85
SiO ₂ (fused gel)	Al ₂ O ₃ (coprecip.)	Var., <40% Al ₂ O ₃	$\Delta = 0.12$ (mole % Al ₂ O ₃)	73
SnO ₂ (mineral)	Fe ₂ O ₃ + "soluble base"	Unknown	< +4.7	56
				70

B. Adsorbed Impurities (Present in Electrolyte before Experiments)

Substrate	Impurity	Impurity level, M	Δ IEPS*	Ref.
Al ₂ O ₃	H ₂ PO ₄ ⁻	~5 × 10 ⁻⁴	~ -4	21
Al ₂ O ₃	SO ₄ ²⁻	~5 × 10 ⁻⁴	~ -2.0	76
TiO ₂	Cl ⁻	~10 ⁻³	~ -1.2	6
TiO ₂	Cl ⁻	~10 ⁻³	~ -2.0	6
TiO ₂	SO ₄ ²⁻	~10 ⁻³	~ -0.7	97
TiO ₂	Ca ²⁺	> 10 ⁻⁴	> +4.8	97
-FeOOH	La ³⁺	10 ⁻³	+1.4	80
-FeOOH	La ³⁺	10 ⁻³	+2.0	80
-Al ₂ O ₃	Na dodecyl sulfate	~5 × 10 ⁻⁴	Est. -5.4	76
-Al ₂ O ₃	Na octyl sulfate	~2 × 10 ⁻⁴	Est. -2	76
-Fe ₂ O ₃	Dodecylamine	2 × 10 ⁻³	+0.05	58
-Fe ₂ O ₃	Dodecylamine	6 × 10 ⁻³	+0.10	58
-Fe ₂ O ₃	Dodecylamine	10 × 10 ⁻³	+0.28	58
-SiO ₂	DTAB [†]	2 × 10 ⁻³	Est. +5	81
-SiO ₂			Est. +4.6 ± 1.5	36
-SnO ₂	Na octyl sulfate	2 × 10 ⁻⁴	Est. -0.7	70
-TiO ₂ (rutile)	Na oleate	~10 ⁻³	Est. -3.7	97

* Δ IEPS > 0 indicates basic shift of IEPs. [†] FeOOH equilibrated with La(NO₃)₃ solution then rinsed once before resp. ^{††} DTAB = dodecyltrimethylammonium bromide. [‡] Each of the alkylamine acetates, C₁₂ (~10⁻³ M), C₁₆ (~5 × 10⁻³ M), C₁₈ (8 × 10⁻³ M), C₂₀ (~10⁻³ M), and C₂₂ (2 × 10⁻³ M) give the indicated Δ IEPS.

be expected to produce a shift by the same mechanism discussed for anions; i.e., should the equivalents of H⁺ lost exceed the equivalents of Mⁿ⁺ adsorbed, the IEPs would shift to a more acid pH.

The effects of various structural or adsorbed impurities on the IEPs of several oxides are summarized in Table VII. The expected shifts are observed.

Specific adsorption of disolvable species exceeding a monolayer can be expected to shift the IEPs to or toward that of the adsorbate. The best example is the adsorption of proteins (1, 12) which shifts the IEPs completely to that characteristic of the adsorbate in each case.

4. Nonstoichiometry, Defect Structures, and Semiconductors

Pravdic and Sotman (96) reported the only work that has been done on variation of IEPs with reasonably well-defined deviations from stoichiometry. The variation of IEPs with the mole ratio of oxygen to uranium (O/U) in the series UO₂-U₂O₅ is shown in Figure 1. The data of Ferreira and Ottewill (88) with natural pitchblende (intermediate between UO₂ and U₂O₅) have been plotted on the same figure using an O/U ratio (= 2.8) reported (84) for material from the

same source. The IEPs shift acid as the oxidation state increases, as would be predicted from the change in Z/r ratio. The points marked "calculated" in Figure 2 were obtained using Eq. 2c to be developed below.

It might be expected that simple heat treatment of some oxides, such as TiO₂, SnO₂, and MnO₂, would result in superficial loss of oxygen and, consequently, nonstoichiometry. This has been observed for TiO₂ (84) and interpreted as production of Ti₂O₃ in the surface. A shift of IEPs in the direction appropriate for the oxidation state produced would be expected quite apart from dehydration effects because the average Z/r changes. There is at present very little evidence in support of this point. However, a preliminary attempt (86) gave the following results which do show the correct trend.

Precipitated TiO ₂ (hydrous rutile)	IEPS
Fpt. heated to 975°, 2 hr.	IEPS = 5.0
Fpt. heated in 10% H ₂ , 975°, 0.5 hr.	IEPS = 5.3
Fpt. heated in 10% H ₂ , 975°, 2 hr.	IEPS = 5.6

The loss of oxygen and IEPs shift could be explained equally well by assuming that oxygen vacancies and n-type semiconductivity result from heat treatment. An n-type semiconductor would be expected to exhibit

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 13/23

188

GEORGE A. PARKS

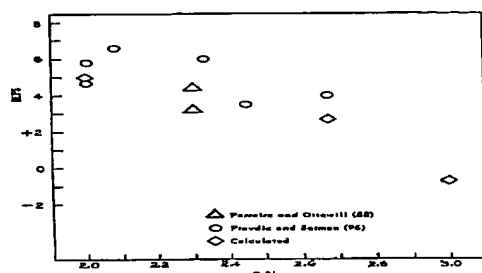


Figure 1.—The effect of composition on the IEPS of uranium oxides.

a more basic IEPS than predicted for the stoichiometric oxide owing to stabilization of adsorbed H^+ by mobile electrons. Similarly p-type semiconductors might be expected to exhibit a more acid IEPS than predicted owing to repulsion of H^+ or stabilization of adsorbed OH^- . Those effects on the IEPS have apparently not been studied to any significant extent.

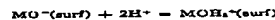
The hydrous oxides precipitated from metal salt solution are defect structures containing a high concentration of structural defects and excess H_2O in addition to coprecipitated ions (124). Schuylenborgh, Arens, and Slinger (110–118) in a painstaking study of aluminum and iron oxides and hydroxides were able to show that any feature of sample history leading to increased crystal perfection (observed by X-ray diffraction line narrowing) leads to decreased IEPS. As discussed under "Effects of Hydration," substitution of H_2O for O^{2-} or OH^- would be expected to shift the IEPS to a more basic pH. A cation vacancy should have the same effect because hydrogen ions would be accepted to make up the charge deficiency resulting in an increased effective OH^-/O^{2-} ratio. Presumably, aging results in loss of excess molecular H_2O and combination of substitutional H^+ with excess OH^- to form H_2O which is subsequently lost (122, 124) resulting in the acid shift of IEPS observed.

C. VARIATION OF IEPS WITH CATIONIC SIZE AND CHARGE

1. An Electrostatic Model

In examining the IEPS data to detect expected trends with cationic size and charge, advantage has

been taken of the postulated analogous dissociation behavior of surface $-MOH$ groups and dissolved molecular hydroxides and oxyacids. Kossakoff and Harkov (62, 77) found it possible to quantitatively account for the strength of oxyacids using a purely electrostatic model of the acid dissociation process. The important variables are the formal charge of the cation, the number of nonhydroxyl oxygen ions (m/n or the hydration state), and the geometrical arrangement of the ions (77). A similar but less thoroughly developed analysis based on the amphoteric dissociation model for the origin of surface charge has been found useful. Equilibrium between positive and negative surface sites involving $2H^+$, i.e.,



is assumed to involve primarily the electrostatic work gained by the approach of $2H^+$ to MO^- . As a first approximation, each ion (the two hydrogen ions are treated as a doubly positive entity) is assumed a point charge separated from the others by average oxide ionic radii (40) (the radius of O^{2-} is taken as 1.40 Å) in a linear array. The free energy involved is then (9a, 92)

$$-\Delta F = -2Z_H Z_O (e^-)^2 / (2r_O) + 2Z_H Z_O (e^-)^2 / (2r_H + r_O) + \Delta F' = RT \ln K \quad (Eq. 1)$$

or, since

$$K = \frac{(MOH_2^+)}{(H^+)^2(MO^-)} = \frac{1}{H^+}; \quad (MDH = IEPS) \quad (Eq. 2)$$

where $\Delta F'$ = non-Coulombic contributions to the hydrogen ion binding energy; A, B, D = constants; Z = ionic charge of species indicated by subscript $H = H^+, O = O^{2-}$, $+$ = cation; ϵ = appropriate dielectric constant of water; e^- = electronic charge; r = ionic radius, $R = 2r_O + r_H$; $(\)$ = ionic concentration or activity. Equation 2 predicts that the IEPS should vary linearly with Z/R , increasing as Z/R decreases. The prediction is roughly verified in Figure 2, a plot of IEPS vs. Z/R .

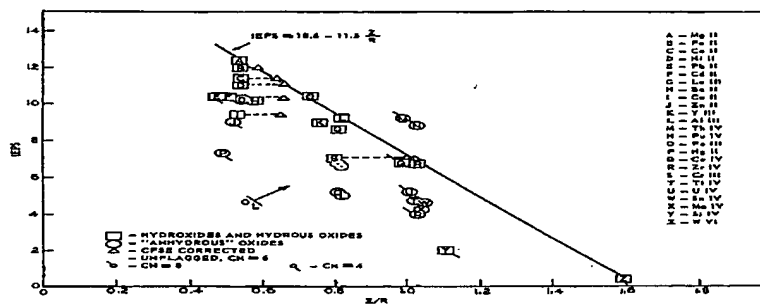
Such a simple electrostatic model cannot apply accurately for several reasons: (1) Crystal field effects increase the stability of the $M-OH$ bond (9b), decreasing the IEPS by reducing the basicity of the group. The crystal field stabilization energy (CFSE) contributes to the term $\Delta F'$ in Eq. 1. (2) The contributions of additional coordinating anions constitute a different constant term for each coordination number. (3) The value of A in Eq. 2 is different for each value of the ratio m/n of nonhydroxyl to hydroxyl oxygens. The exact hydration state of solids for which IEPS's are available is usually not known; hence, it is possible only to consider two extremes, hydrous and anhydrous, using the term "hydrous" in the generic sense described earlier.

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 14/23

ISOELECTRIC POINTS OF SOLID OXIDES AND HYDROXIDES

189

Figure 2.—The relationship between IEPS and Z/R .

It is feasible to account for these effects analytically, but this refinement is unwarranted at present. Instead, the constants A and B of Eq. 2 will be evaluated separately for each coordination number and hydration extreme, and the CFSE correction will be evaluated for each transition metal ion by analogy with calculations of simple electrostatic and CFSE terms in the hydration energies of these ions.

2. Coordination Number Six and Crystal Field Effects

Among IEPS values for the hydroxides and hydrous oxides with coordination number six (126, 127) the IEPS's of $\text{Al}_2\text{O}_3(\text{hyd})$ and $\text{MgO}(\text{hyd})$ are most trustworthy. These two oxides require no crystal field correction and are the least likely to involve important covalent bonding. The constants in Eq. 2, evaluated using these two points are: $A = 18.6$; $B = 11.6$. Equation 2 is plotted in Figure 2. The points representing $\text{La}_2\text{O}_3(\text{hyd})$, $\text{Fe}_2\text{O}_3(\text{hyd})$, and $\text{WO}_3(\text{hyd})$ which also involve no large CFSE correction fall very close to the line, indicating that the equation is valid over 12 orders of magnitude in H^+ concentration.

As expected, the IEPS's of the transition metal hydroxides are not described by Eq. 2 in this form. The crystal field contributions to the hydration energies of these ions have been calculated (9b,c). The CFSE in the hexaquo ions corresponds to a weak crystal field. The field is still weaker if the cation is coordi-

nated with OH^- rather than H_2O (9b,d). Hence the relative magnitudes of CFSE should be the same in the hydroxides as in the hexaquo ions. We will assume that the crystal field contribution to the OH^- binding energy in the hydroxides and hydrous oxides, etc., is proportional to that calculated for the hexaquo ions. The appropriate energies, scaled from figures in Basolo and Pearson (9c), are listed in Table VIII.

Equation 2 may be rewritten to take the CFSE into account as

$$\text{IEPS} = A - B(Z/R) - C(\text{CFSE}) \quad (\text{Eq. 2a})$$

or

$$\text{IEPS} = 18.6 - 11.5 \left[\frac{Z}{R} + \frac{C}{11.5} (\text{CFSE}) \right] \quad (\text{Eq. 2b})$$

The quantity $(C/11.5)(\text{CFSE})$ in Eq. 2b may be regarded as an effective change in Z/R necessary to account for the CFSE contribution to ΔF . The constant $(C/11.5)$ was arbitrarily evaluated using the IEPS for $\text{Ni}(\text{OH})_2$. The result, $(C/11.5) = 0.0029$, was then used to calculate $(Z/R)_{\text{eff}}$ for the other transition metals, in some cases making possible predicted values where no measurements are available. The results are summarized in Table VIII. The validity of this approach is amply demonstrated by comparison of columns 6 and 7 in Table VIII and study of Figure 2. In Figure 2, plotting IEPS against $(Z/R)_{\text{eff}}$ brings the points for all the hydrous transition metal oxides or

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 15/23

190

GEORGE A. PARKS

TABLE VIII
CRYSTAL FIELD CORRELATIONS TO $(Z/R)_{eff}$

Ion	Approx. CFSE for M^{n+} (a.u.) ^a	$\Delta E/R$ ^a	Z/R (40)	$(Z/R)_{eff}$ ^b	Predicted IEPS ^c for hydroxide or hydrous oxide	Measured IEPS (hydrous materials)
Mn ²⁺	0	0	0.34	0.34	12.4	...
Mn ³⁺	42	0.12	0.79	0.91	8.1	...
Fe ²⁺	18	0.05	0.66	0.89	11.8	12
Fe ³⁺	0	0	0.61	0.61	9.3	8.8
Co ²⁺	33	0.10	0.54	0.64	11.2	11.4
Co ³⁺	42	0.12	(0.81) ^d	(0.93)	7.0	[11.1]
Ni ²⁺	42	0.12	0.54	0.66	[11.0]	...
Ni ³⁺	(30)	0.09	(0.81)	(0.90)	8.6	...
Cu ²⁺	39	0.11	0.53	0.64	11.2	9.4
Sc ³⁺	0	0	0.77	0.77	11.3	...
Cr ²⁺	72	0.20	(0.50)	(0.70)	10.0	...
Cr ³⁺	70	0.20	0.60	1.00	7.1	7.0
V ²⁺	73	0.21	(0.54)	0.75	10.0	...
V ³⁺	39	0.11	0.78	0.89	8.4	...
Ti ²⁺	39	0.10	(0.59)	(0.72)	10.3	...
Ti ³⁺	30	0.09	0.78	0.87	8.6	...

^a $\Delta E/R = 0.0029(CFSE)$. ^b $(Z/R)_{eff} = Z/R + \Delta E/R$. ^c From Eq. 2b. ^d Entries in parentheses are estimates. ^e ~ 9.0 for FeO₂ from nitrate hydrolysis, see Table III. ^f Entries in brackets were used to evaluate constants in Eq. 2b.

hydroxides except that for Cu(OH)₂ onto the line representing Eq. 2a.

While the coordination number (CN) of Cu(II) in the hydroxide has been assumed to be six in accord with the structures of several oxyhydroxides (125b), the hydroxide is unstable relative to the oxide in which Cu(II) is found in square-planar oxygen coordination (126b). The CFSE for Cu(II) in square-planar coordination should be larger than has been used for octahedral coordination (6c), hence the failure of this one point to correlate with $(Z/R)_{eff}$ can be understood.

We have seen that oxide IEPS's are more acidic than the corresponding hydroxides or hydrous materials. A straight line of slope 11.5 can be fitted to the points representing oxides with CN = 6. Its intercept, $A = 18.5$, reflects the average IEPS differences between oxides and hydroxides of about 2 pH units observed in Table VI.

8. Coordination Number Four

The hydrous and "anhydrous" materials with CN = 4 can be fairly well represented by Eq. 2a if A has the values 18.0 and 13.9, respectively. Thus the average IEPS shift due to hydration is about 2.1 pH units as it is for CN = 6. The average differences in IEPS between materials of CN = 6 and those with the same Z/R but with CN = 4 is about 2.6 pH units.

4. Coordination Number Eight

Because additional anions increase the binding energy of H⁺ to the -MOH group, a change of CN from 6 to 8 should increase the IEPS. The IEPS's for "anhydrous" ThO₂ and PuO₂ can be accounted for by assigning $A \approx 20.7$.

The data for CeO₂, UO₂, and ZrO₂ are better described by Eq. 2b if $A = 18.6$ as for hydrous materials of CN

= 6. Inasmuch as the description of these materials indicates that UO₂ and ZrO₂ should be classed among "anhydrous" materials, the assignment of a value to A for this entire group must remain tentative.

6. Summary

In order to make possible a convenient graphical test of the validity of Eq. 1 and 2 they can be expressed in the alternate forms

$$IEPS = A_{eff} - 11.5(Z/R + 0.0029(CFSE)) \quad (\text{Eq. 2e})$$

and

$$IEPS = 18.6 - 11.5(Z/R + 0.0029(CFSE)) + a \quad (\text{Eq. 2f})$$

or

$$IEPS = 18.6 - 11.5(Z/R)_{eff} \quad (\text{Eq. 2d})$$

where

$$(Z/R)_{eff} = (Z/R + 0.0029(CFSE)) + a$$

Changes in A arising from changes in CN or hydration are expressed as an effective change in Z/R in Eq. 2d.

The IEPS's are plotted vs. $(Z/R)_{eff}$ in Figure 8. In roughly 67% of the cases plotted, the experimental IEPS falls within 1 pH unit of the line representing Eq. 2d. In all cases the IEPS predicted with Eq. 2e is within 0.5 pH unit of the maximum observed value.

From the success of Eq. 2d it is concluded that a simple electrostatic model describes quite well the mechanism by which "oxide" surfaces are charged in aqueous solutions and that Eq. 2e, with appropriate values of A , may be used with reasonable confidence to predict the IEPS of simple oxide materials. Predictions involving CN = 8 should be made with reservations. The values of the constants A and a appropriate for each coordination number are summarized in Table IX.

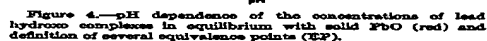
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191



III. THE ISOELECTRIC POINTS OF AQUEOUS

The stability constants for a number of metal hydroxo complexes have been determined and calculated for the complex isoelectric points (IEP) and several other equivalence points (EP) for each system. An equivalence point (EP) is the pH at which any selected pair of species are present in equal concentrations. Equivalence points. The selected ions, if hydroxo complexes, are indicated simply by a pair of numbers in parentheses, the first indicating the ionic charge of the positive ion, the second the charge of the negative ion. For example, EP(+1, -1) is the pH at which $(M^{++}(OH)_2)^{+1} = (M^{+}(OH))^{0}$ and, because the concentrations of these two species are small, is usually essentially equal to the pK_a of the M^{++} ion. The EP(+1, -2) is the pH at which $(M^{++}(OH)_2)^{+1} = (M^{+}(OH)_2)^{-1}$ and is identical with the IEP. The EP(+1, -3) is the pH at which $(M^{++}(OH)_2)^{+1} = (M^{+}(OH)_3)^{-2}$.



which $4(M^{++}(OH)_{3-4}^{--}) = (M^{++}(OH)_{2+1}^{-})$. The $EP(3,OH)$ is the pH at which $3(M^{++}(OH)_{3-4}^{--}) = (OH^{-})$. The relationships among the IEP's and the various EP's are illustrated in Figure 4 where the concentrations of mononuclear hydroxo complexes in equilibrium

MAY. 30. 2003 9:25AM Mail 1+650-812-3575 INFO EXPRESS

NO. 1980 P. 17/23

102

GEORGE A. PARKS

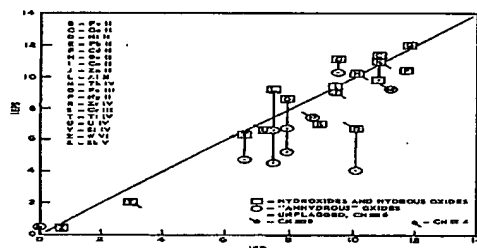


Figure 5.—The relationship between IEPs and IEP.

with PbO are plotted as functions of pH. The IEP's and EP's are collected in Table X. In the first and second columns the IEP and EP(2.1) extremes resulting from consideration of all cited literature are given as the lower entry for each element. A preferred value is given as the upper entry. These were selected by assuming Feitknecht and Schindler (29) standard and selecting additional data where necessary from authors they had chosen. Failing in this, an author was chosen who reported a K very near one selected by Feitknecht and Schindler as well as one sought, usually $K_{(2.1)}$. In other columns the meaning of multiple entries is the same unless indicated otherwise.

IV. COMPARISON OF THE ISOELECTRIC POINTS OF SOLIDS WITH THOSE OF HYDROXO COMPLEX SYSTEMS

A. GENERAL OBSERVATIONS

The IEP's are compared with corresponding IEP's in Figure 5. It is obvious that the two quantities are related, especially for the hydrous oxides and hydroxides; however, detailed comparison of each IEPs and all of the corresponding EP's, immediately reveals that in many cases the IEPs is more closely approximated by an EP other than the IEP. Table XI lists the materials studied in groups according to the EP which most closely matches the IEPs. Where several IEPs are reported in Table I, the value selected for comparison in Table XI is given in parentheses.

After study of the properties of the materials in each group, several trends emerge: (a) all materials for which IEPs = IEP are hydrous and most have CN = 6 (those in this group with CN = 6 have CN = 4 and $r_+ < 1.0$ Å); (b) with the exception of HgO, the

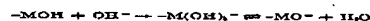
materials for which IEPs = EP(1,OH) are either hydrous with CN = 4 and $r_+ > 1.0$ Å, or are "anhydrous" oxides which rehydrate very slowly once thoroughly dehydrated; (c) materials for which IEPs = EP(2,OH) are all "anhydrous" oxides which in most cases exhibit at least one other IEPs.

B. ADSORPTION AND IDENTIFICATION OF POTENTIAL-DETERMINING SPECIES

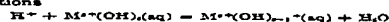
The observations of the previous paragraph can be explained if it is postulated that: (a) H^+ , OH^- , and all hydroxo complexes present play important roles in establishing surface charge and are potential-determining ions (PDI) (45); (b) all hydroxo complexes adsorb onto oxide materials physically with about equal equilibrium constants in each case; and (c) H^+ and OH^- adsorb physically or nondissociatively on some materials and chemically or dissociatively on others. Dissociative adsorption involves dissociation of surface -MOH groups, e.g.,



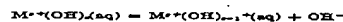
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with equilibrium constants determined by the cation M and assumed nearly equal to those for the analogous reactions



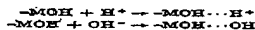
or



and

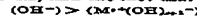


Nondissociative or physical adsorption involves no dissociation of surface -MOH groups and is assumed to be governed by equilibrium constants nearly equal to those for adsorption of hydroxo complexes and the same for H^+ and OH^- . The adsorption reactions can be represented by



The IEPs is thus equal to the IEP if the PDI, as determined by relative concentrations, is any pair among H^+ , OH^- , $M^{n+}(OH)_{n-1}$, and $M^{n+}(OH)_n$, provided H^+ and OH^- adsorb dissociatively. The equivalence of H^+ and $M^{n+}(OH)_{n-1}$ as PDI arises because development of a positive site by surface dissociation or by formation in solution and subsequent adsorption of a monovalent complex are indistinguishable processes.

The near equality of IEPs and IEP for materials in column 1, Table XI, and the fact that for most systems



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	ISF = EP(1,1)	EP(1,1)	EP(1,0H)	EP(0,1H)	EP(0,1H)	Ref.
Al(III)*	7.5	0.2	7.3 (Al(OH) ₃)	Al- 5.8	5.9	4, 8, 13, 17, 25
SB(III)	(5.2-7.7)	7.7 amorph	25, 29, 33, 42, 05
SB(V)	5-5.5	73, 94, 105, 107
Bo(II)	10.1	(0.0-7.9)	0.8 (inact.)	0.0	57, 93
Cd(II)	(9.0-10.4)	11.7	10.2 (act.)	7	0.4 (inact.)	18, 29, 65
Cr(III)*	(11.4-12.3)	(10.8-11.2)	4.3 (act.)	0.0 (act.)	13, 29, 41, 70, 128
Co(II)*	(8.2-9.5)	(7.8-8.0)	8.2	7.8	6.5-7.0	18, 29, 29, 05
Cu(II)*	10.8	10.5	4.2 (pink Cu(OH) ₂)	8.9	13, 29, 118
Cu(II)	(6.0-11.8)	(7.8-11.8)	0.0 (blue)	0.4	7.3 (CuO)	13, 29, 43, 90, 128
Fe(II)*	9.4	7.0	7.0	7.9 (Cu(OH) ₂)	0.1	18, 29, 40, 65
Fe(II)*	(11.8-12.4)	(10.5-11.5)	9.0 (inact.)	0.1
Fe(III)*	8.0	0.4	10.4 (act.)	0.8	4.7 (-Fe(OH) ₃)	11, 30, 40, 06, 109,
Fe(III)*	(7.4-8.4)	(5.6-6.7)	5.7 ("act. Fe(OH) ₃ ")	4.8-4.9	5.0 (-Fe(OH) ₃)	128
Fe(III)*	10.8	0.8	10.0 (red FeO)	8.0	4.0 (-Fe(OH) ₃)	13, 29, 05, 94, 128
Mn(II)	(6.0-11.1)	(0.4-0.8)	10.1 (cr. FeO)	9.0	4.8 ("act. Fe(OH) ₃ ")
Hg(II)	11.8	11.8	10.3 (Fe(OH) ₃)	0.1	13, 29
Mo(VI)*	8.0	7.1	9.0	0.7	13, 29
Ni(II)*	(8.4-9.4)	(5.8-7.2)	(6.3-7.1)	5.0	40, 65, 115
Si(IV)*	(9.0-10.3)	9.6	8.5 (act.)	8.4	13, 10, 20, 94, 05,
As(III)	(2.8-5.2)	7.4 (inact.)	9.2	EP(II,1) = 5.2-5.7	116
Sn(IV)	12.1	18, 14, 18
Ta(IV)*	(12-12.9)	29, 27
Ta(IV)*	12.9
Ta(IV)*	(3.8-4.2)	60
Sn(II)	~8.1	~8.9	~7.8	~6.4	50
Ti(IV)*	7.3	5.8	7.1	5.4	13, 29, 88
U(VI)*	(6.4-7.3)	(6.2-5.8)	13, 23, 29, 85
U(VI)*	(5.6-7.1)	5.6	-0.8 (rutile)	0.4	18, 29, 05, 06, 94
W(VI)*	(9.0-9.8)	(8.6-5.8)	4.7 (amorph.)	3.7
W(VI)*	(1.0-3.5)	(7.3-7.8)	(7.7-6.0)	6.7	13, 30, 48
Zn(II)*	(0.4-1.0)	27, 106
Zn(II)*	10.0	9.4	8.6 (ZnO)	8.0 (ZnO)	27, 49
Zn(II)*	(8.7-10.6)	(8.5-9.8)	5.0 (Zn(OH) ₂ amorph.)	5.0 (Zn(OH) ₂ amorph.)	18, 29, 01, 02, 108
Zn(II)*	(9.8-10.6)	(7.2-7.6)	7.8	7.8

$\gamma\text{-Al}_2\text{O}_3$ (8.5, 10.6) (7.2, 7.6) 7.8 6.8 18.29, 61, 65, 94
 Several values of ΔH_f are available as pHMS data estimated graphically. For $\gamma\text{-Al(OH)}_3$, 7.7 (42); for "amorph. Al(OH)_3 ", 7.3 (73); for Al(OH)_3 (187); for $\gamma\text{-Al(OH)}_3$, 7.3 (73); for "hydrous oxide", 7.2 (101). If surface structure changes from amorphous on acid side to boehmite on basic side, ΔH_f can be based on boehmite (73). If surface structure changes from amorphous on acid side to $\gamma\text{-Al(OH)}_3$ on basic side, ΔH_f can be based on $\gamma\text{-Al(OH)}_3$ (73).
 ΔH_f (kJ/mole) = $9.83(3.6) - \log^* K_{sp}$, i.e. $\log^* K_{sp}$ = $-8.8(18)$. If surface structure changes from amorphous on acid side to $\gamma\text{-Al(OH)}_3$ on basic side, ΔH_f can be based on $\gamma\text{-Al(OH)}_3$ (73).
 pHMS in 0.1 M LiCl, 20°C, $\log^* K_{sp}$ = $10.12(16; 30, 810)$. pHMS data supplemented by hydrolytic data.
 pHMS in 0.1 M LiCl, 20°C, $\log^* K_{sp}$ = $10.12(16; 30, 810)$. pHMS data supplemented by hydrolytic data.
 (18, 20, 61), Σc^+ dominant (18, 20, 65), $\log^* K_{sp}$ = $10.12(16; 30, 810)$. pHMS data supplemented by hydrolytic data.
 (18, 20, 61), Σc^+ dominant (18, 20, 65), $\log^* K_{sp}$ = $10.12(16; 30, 810)$. pHMS data supplemented by hydrolytic data.

Imply that all hydrous materials with $ON = 6$ or $CN = 4$ if $r < 1.0 \text{ \AA}$ involve as PDI the ions $M^{+2}(OH)_{2-1}$ and OH^- and the OH^- adsorbs dissociatively. Because H^+ and $M^{+2}(OH)_{2-1}$ are identical and the two negative PDI for these materials, OH^- and $M^{+2}(OH)_{2-1}$, are also equivalent, the IEPS is equal to IEP regardless of whether or not hydroxo complexes are present.

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NO. 1980 P. 19/23

194

GEORGE A. PARKS

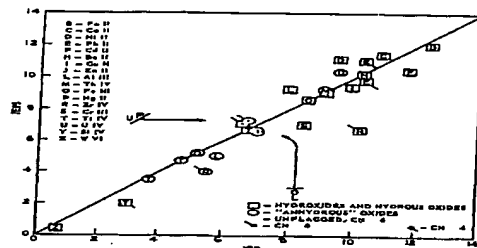


Figure 6.—The relationship between IEPS and selected EP.

TABLE XI

EQUIVALENCE POINTS MOST CLOSELY APPROXIMATING THE ISOELECTRIC POINT OF A SOLID OXIDE MATERIAL

IEPS ~ EP	IEPS ~ EP	IEPS ~ EP	IEPS ~ EP
(1)	(2)	(3)	(4)
Fe(OH) ₃	Be(OH) ₂	Ta ₂ O ₅ (9.5)	Al ₂ O ₃ (hydrated) (9.5)
Co(OH) ₂	ThO ₂ (hydrated)	SnO ₂ (7.0)	Fe ₂ O ₃ (hydrated) (9.5)
Ni(OH) ₂ , NiO	SnO ₂ (hydrated)	TiO ₂ (8.2)	
Cr(OH) ₃ , Cr ₂ O ₃	Na ₂ O (9.0)	Al ₂ O ₃ (9.0)	
Cr ₂ O ₃ (hydrated)	Al ₂ O ₃ (9.0)	Fe ₂ O ₃ (9.0)	
Fe ₂ O ₃ (hydrated) (9.5)	Fe ₂ O ₃ (9.5)	Fe ₂ O ₃ (9.5)	
Cr ₂ O ₃ (hydrated)	TiO ₂ (8.7)	Fe ₂ O ₃ (9.7)	
TiO ₂ (hydrated) (9.5)			
WO ₃ (hydrated)			
SiO ₂			

In general, IEP > EP(+, OH) > EP(2, OH).

both only slightly soluble, and very slow to come to equilibrium. Both of these materials have one reported IEPS near pH 7. Unfortunately, no experimenter has reported even the total metal concentration in solution during measurement of IEPS.

Table XII summarizes the probable PDI and IEPS-EP relationships for the two classes of materials in the

first and second columns of Table XI. The IEPS's are compared in Figure 6 with EP's selected using the "rules" of Table XII.

C. ALTERNATE MECHANISMS FOR POTENTIAL-DETERMINING ION ADSORPTION

1. Adsorption onto Hydrogen-Bonded Water

Another possible adsorption mechanism may prove useful in the explanation of the postulated nondissociative adsorption. It is well established, particularly for SiO₂ gels (4, 78), that the first layer of adsorbed water is present as —MOH groups and that the second layer is hydrogen bonded to the first. Thus arrays such as —MOH⁺ should be present on immersed surfaces. Dissociative adsorption of H⁺ or OH⁻ onto this group, because interactions with M²⁺ in this case is a second-order effect, should reflect the charge and size of M²⁺ only slightly, hence be nearly indistinguishable from the postulated physical or nondissociative adsorption onto —MOH groups.

2. Nonequivalence of Potential-Determining Species

It is conceivable that hydroxo complex ions other than those which are most concentrated near the IEPS could usurp the dominant potential-determining role.

Raupach's (99) study of the solubility of aluminum oxyhydroxides and hydroxides led him to believe that the predominant ion in equilibrium with α-Al(OH)₃ and γ-AlOOH is Al(OH)₄⁻ and that in equilibrium with "bauxite" and γ-AlOOH or "precipitated Al(OH)₃" is Al(OH)₃⁺. Without giving physical reasons, he proposed a mechanism by which the solution is depleted in Al³⁺, leaving Al(OH)₄⁻ the predominant potential-determining ion in the appropriate systems.

Each element listed below has at least one IEPS (reported by more than one author) which is more closely approximated by EP(2, OH) or EP(2, 1) than by the IEP or EP(1, OH).

Al(III) IEPS = 5	EP(2, OH) = 5.8	IEP = 7.6
Fe(III) IEPS = 5.7	EP(2, OH) = 6.4 (5.9-6.7)	IEP = 8.0
Th(IV) IEPS = 9.5	EP(2, 1) = 8.9	IEP = 11.7

TABLE XII

SUMMARY OF PROBABLE POTENTIAL-DETERMINING IONS AND EQUIVALENCE POINTS—ISOELECTRIC POINT

Description of solid	RELATIONSHIPS FOR TWO CLASSES OF SOLIDS	Hydroxide complexes present	Hydroxide complexes absent
A. Hydroxides, oxyhydroxides, hydrous oxides, and superficially hydrated or hydrous oxides. CN = 6 and CN = 4 if $r_+ < 1.0 \text{ \AA}$.	PDI are M ²⁺ (OH) ₂ or H ⁺ and M ²⁺ (OH) ₂ or OH ⁻ IEP = IEPS (dissociative adsorption)	PDI are H ⁺ , OH ⁻ IEP = IEPS (dissociative adsorption)	
P. "Amorphous" oxides and class "A" materials with CN = 4 and $r_+ > 1.0 \text{ \AA}$.	PDI are same as class "A" and EP(+, OH) or EP(+, -) = IEPS (nondissociative adsorption)	PDI are H ⁺ , OH ⁻ IEPS ~ pH 7 (nondissociative adsorption)	

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ISOELECTRIC POINTS OF SOLID OXIDES AND HYDROXIDES

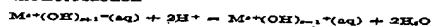
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TR(IV) IEPs = 8.5 EP(2,OH) = 5.7	IEP = 6.5
Zr(IV) IEPs = 4.0 EP(2,OH) = 5.5	IEP = 10.2
Zr(IV) IEPs = 6.7 EP(2,1) = (7.2-7.0)	IEP = 10.2

Of these, the IEPs of Al(III), Th(IV), and Zr(IV) also fail to correlate with $(2/F)^{1/2}$. This point and the coincidence that this particular IEPs = IEP(2,OH) or EP(2,1) do seem to indicate that a different mechanism is operating to establish equilibrium between the solid and the liquid in these cases. However, neither realistic justification for the fact nor physical reasoning upon which to base selection of the exclusive potential-determining role of $M^{++}(OH)_{2-}$ has yet been found.

3. pH-Dependent Surface Modification

Raupach (99, 100) also found that the acid solubility of the oxyhydroxides and hydroxides of aluminum was characteristic of α -Al₂O₃ or amorphous Al(OH)₃ (α -AlOOH?) while the solubility in basic solutions was characteristic of γ - or δ -Al(OH)₃. This may reflect recrystallization of the surface accompanying the change in pH. (The relative stability of FeOOH and Fe₂O₃ is pH dependent. The reaction is slow in bulk but presumably occurs quickly at the solid-solution interface (117).) Normally the IEP is independent of the state of hydration or crystalline modification of the solid phase because the free energy terms representing the solid cancel in calculation of the equilibrium constant for the net reaction



However, if the structure or composition of the solid or its surface change with pH, the change must be reflected either in the ionic concentrations used with the equilibrium constant for this reaction or in calculation of the constant itself by taking into account the free energy involved in the solid change. For the Al(III) system, the IEP is pH 5.2 if calculated on the assumption that Al(OH)₃⁺ is produced through equilibration of the solution with an amorphous hydroxide surface and that Al(OH)₃⁻ is produced through equilibration with an α -Al(OH)₃ surface. This value is in considerably better agreement with the observed IEPs for Al₂O₃ (hyd) (IEPs = 9.2) than is the nominal IEP (pH 7.5). The most basic IEP calculable in this way for Fe₂O₃ assumes that the surface is amorphous hydroxide when acid and FeOOH when basic. The result, IEP = 9.0, is in excellent agreement with the most basic observed IEPs = 9.0. In spite of the moderate success in these two cases, no physical reason upon which to base prediction of circumstances leading to pH-dependent surface modification nor any direct evidence of such modification is immediately apparent.

V. SUMMARY AND CONCLUSIONS

Extensive lists of isoelectric points of solid oxide materials (IEPs) and of metal hydroxide complex systems (IEP's) have been compiled. The IEPs reflect the chemical composition of the solid and the electrolyte in which it is immersed. Structural or adsorbed anionic impurities shift the IEPs to more acid values, cationic impurities to more basic values or toward the IEPs characteristic of the impurity oxide. Oxidation and reduction resulting in nonstoichiometry may be expected to shift the IEPs toward that characteristic of the oxidation state produced. Hydration increases the IEPs; dehydration and increased structural perfection decrease the IEPs. The IEPs of pure oxide materials can be quantitatively accounted for in most cases by an electrostatic model involving the charge to radius ratio and the coordination number with crystal field and hydration corrections.

The IEPs and IEP are definitely related and are equal for many hydrous materials; however, for a significant number of materials there are other IEP's which more closely approximate the IEPs. There appear to be several mechanisms by which H⁺, OH⁻, and all hydroxide complexes present determine the surface charge on immersed oxide materials. Further work is needed to clarify the factors deciding which mechanism predominates in a given case, but it appears that for some materials adsorption of OH⁻ and $M^{++}(OH)_{2-}$ can be distinguished from amphoteric dissociation of bound MOH groups.

Acknowledgments.—The author is grateful to the U. S. Atomic Energy Commission for financial support under Contract AT-(04-9)326 PA #3. He wishes to express thanks to Drs. F. L. De Bruyn, R. B. Bhappu, H. C. Li, and O. Purcell, and Messrs. G. H. Korpi, E. Volin, and O. L. Flaningham for permission to use unpublished data, and to Dr. G. E. Agar and Messrs. J. H. Anderson, Jr., and G. H. Korpi for painstaking reviews of the manuscript. Dr. de Bruyn deserves special thanks for stimulating initial interest in the subject. The patient typing and proofreading of many drafts by Mrs. O. Bacon and Mr. and Mrs. F. H. Skelding are much appreciated.

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198

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